

What is claimed is

1. A process for the production of polyolefin hollow articles, which comprises

charging the polyolefin with a stabilizer combination, comprising

(a) at least one compound from the group of the organic phosphites and phosphonites,

(b) one or more compounds selected from the group consisting of

i.) hydroxylamine derivatives and

ii.) amine oxide derivatives and

(c) at least one compound from the group of the hindered amine stabilizers,

filling this mixture into a mold, heating this mold in an oven to above 280°C, such that the stabilized polyolefin fuses,

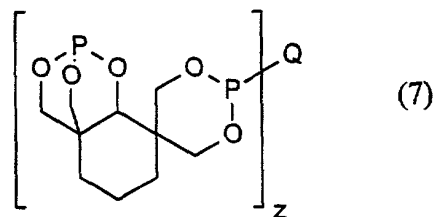
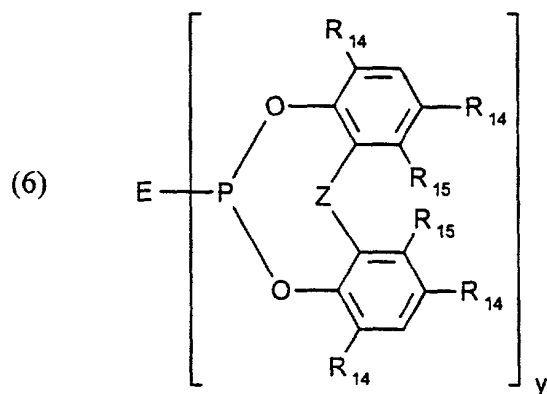
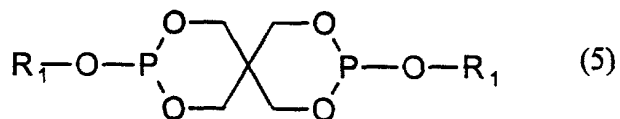
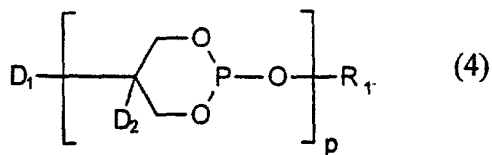
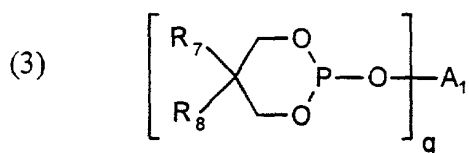
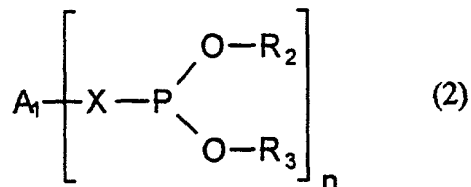
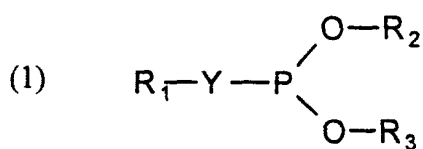
rotating the mold around at least 2 axes, the plastic material spreading to the walls,

cooling the mold while still rotating,

opening it, and

taking the resultant hollow article out.

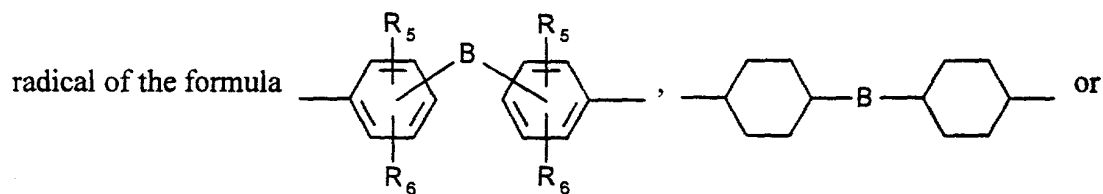
2. A process according to claim 1 wherein the organic phosphites and phosphonites of component (a) are selected from the group consisting of formulae (1), (2), (3), (4), (5), (6) and (7)



in which the indices are integral and

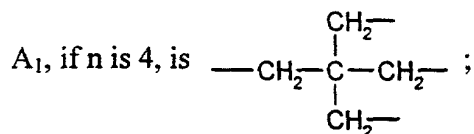
n is 2, 3 or 4; p is 1 or 2; q is 2 or 3; r is 4 to 12; y is 1, 2 or 3; and z is 1 to 6;

A<sub>1</sub>, if n is 2, is C<sub>2</sub>-C<sub>18</sub> alkylene; C<sub>2</sub>-C<sub>12</sub> alkylene interrupted by oxygen, sulfur or -NR<sub>4</sub>-; a



phenylene;

A<sub>1</sub>, if n is 3, is a radical of the formula -C<sub>r</sub>H<sub>2r-1</sub>-;



A<sub>2</sub> is as defined for A<sub>1</sub> if n is 2;

B is a direct bond, -CH<sub>2</sub>-, -CHR<sub>4</sub>-, -CR<sub>1</sub>R<sub>4</sub>-, sulfur, C<sub>5</sub>-C<sub>7</sub> cycloalkylidene, or cyclohexylidene which is substituted by from 1 to 4 C<sub>1</sub>-C<sub>4</sub> alkyl radicals in position 3, 4 and/or 5;

D<sub>1</sub>, if p is 1, is C<sub>1</sub>-C<sub>4</sub> alkyl and, if p is 2, is -CH<sub>2</sub>OCH<sub>2</sub>-;

D<sub>2</sub>, if p is 1, is C<sub>1</sub>-C<sub>4</sub> alkyl;

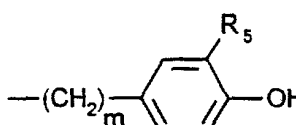
E, if y is 1, is C<sub>1</sub>-C<sub>18</sub> alkyl, -OR<sub>1</sub> or halogen;

E, if y is 2, is -O-A<sub>2</sub>-O-,

E, if y is 3, is a radical of the formula R<sub>4</sub>C(CH<sub>2</sub>O-)<sub>3</sub> or N(CH<sub>2</sub>CH<sub>2</sub>O-)<sub>3</sub>;

Q is the radical of an at least z-valent alcohol or phenol, this radical being attached via the oxygen atom to the phosphorus atom;

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently of one another are C<sub>1</sub>-C<sub>18</sub> alkyl which is unsubstituted or substituted by halogen, -COOR<sub>4</sub>, -CN or -CONR<sub>4</sub>R<sub>4</sub>; C<sub>2</sub>-C<sub>18</sub> alkyl interrupted by oxygen, sulfur or -NR<sub>4</sub>-; C<sub>7</sub>-C<sub>9</sub> phenylalkyl; C<sub>5</sub>-C<sub>12</sub> cycloalkyl, phenyl or naphthyl; naphthyl or phenyl substituted by halogen, 1 to 3 alkyl radicals or alkoxy radicals having a total of 1 to 18 carbon

atoms or by C<sub>7</sub>-C<sub>9</sub> phenylalkyl; or a radical of the formula  in which m is

an integer from the range 3 to 6;

R<sub>4</sub> is hydrogen, C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>5</sub>-C<sub>12</sub> cycloalkyl or C<sub>7</sub>-C<sub>9</sub> phenylalkyl,

R<sub>5</sub> and R<sub>6</sub> independently of one another are hydrogen, C<sub>1</sub>-C<sub>8</sub> alkyl or C<sub>5</sub>-C<sub>6</sub> cycloalkyl,

R<sub>7</sub> and R<sub>8</sub>, if q is 2, independently of one another are C<sub>1</sub>-C<sub>4</sub> alkyl or together are a 2,3-dehydropentamethylene radical; and

R<sub>7</sub> and R<sub>8</sub>, if q is 3, are methyl;

R<sub>14</sub> is hydrogen, C<sub>1</sub>-C<sub>9</sub> alkyl or cyclohexyl,

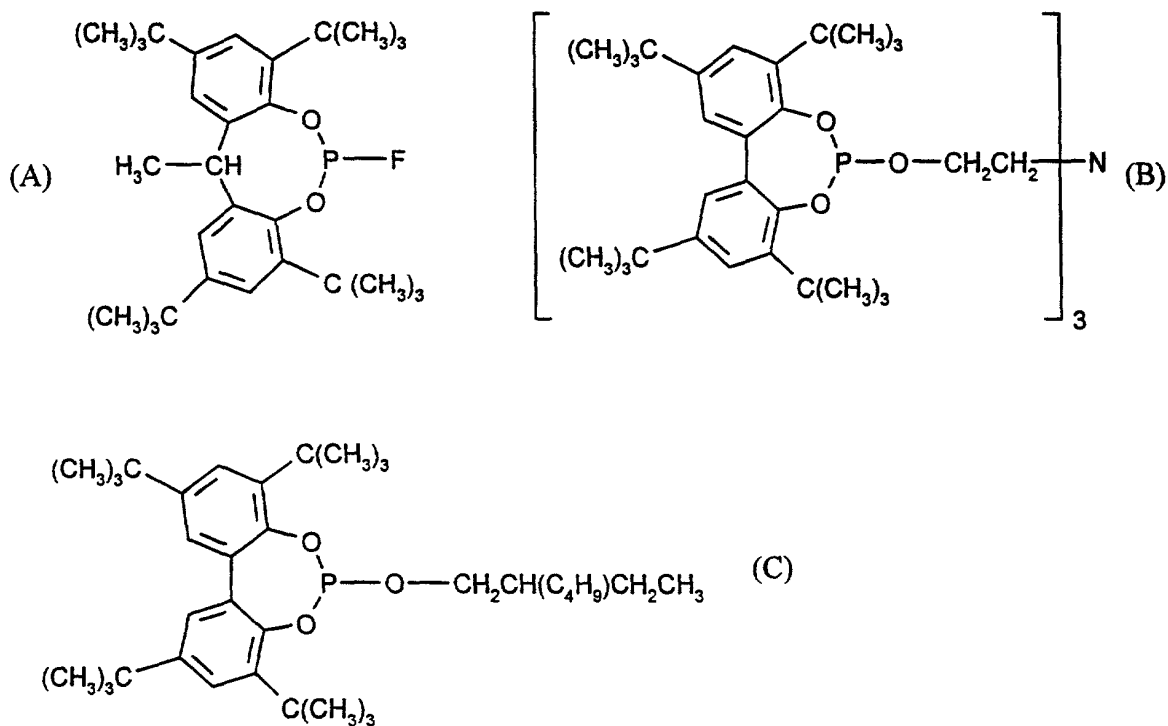
R<sub>15</sub> is hydrogen or methyl and, if two or more radicals R<sub>14</sub> and R<sub>15</sub> are present, these radicals are identical or different,

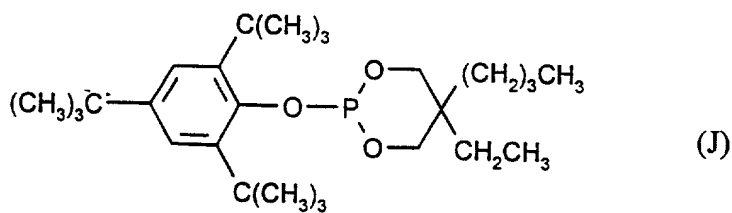
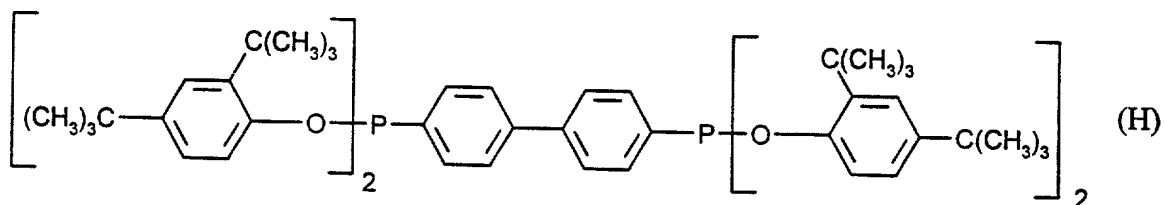
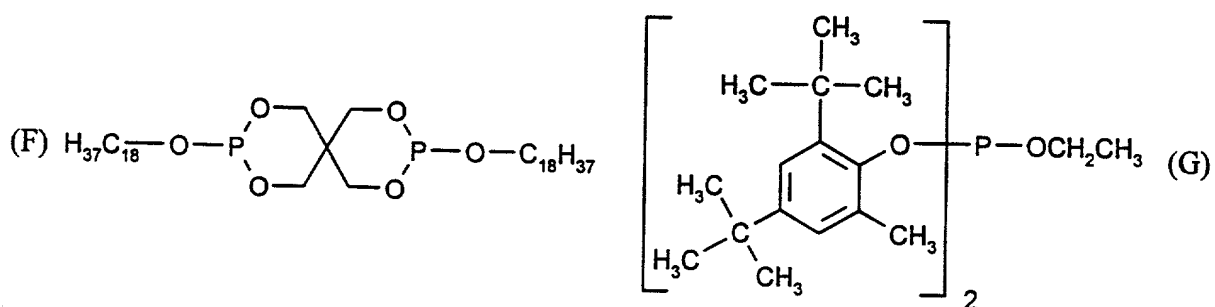
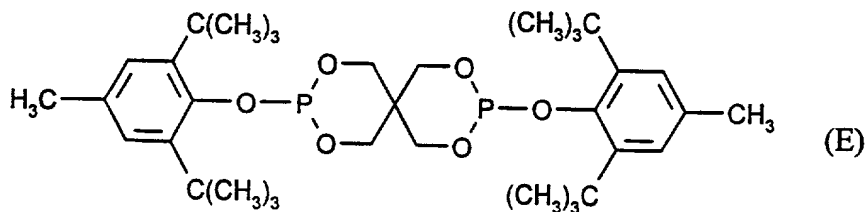
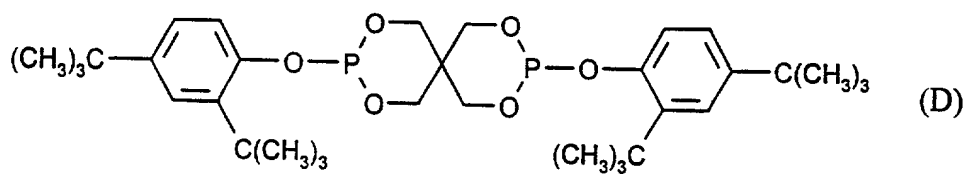
X and Y are each a direct bond or oxygen,

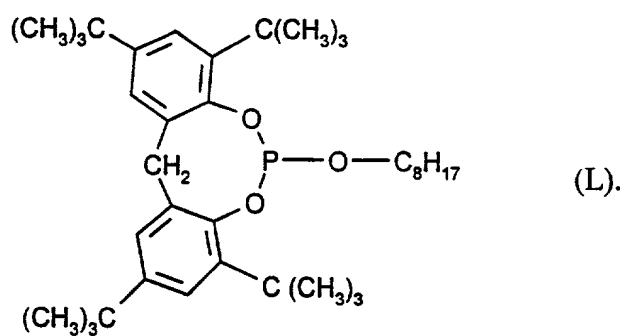
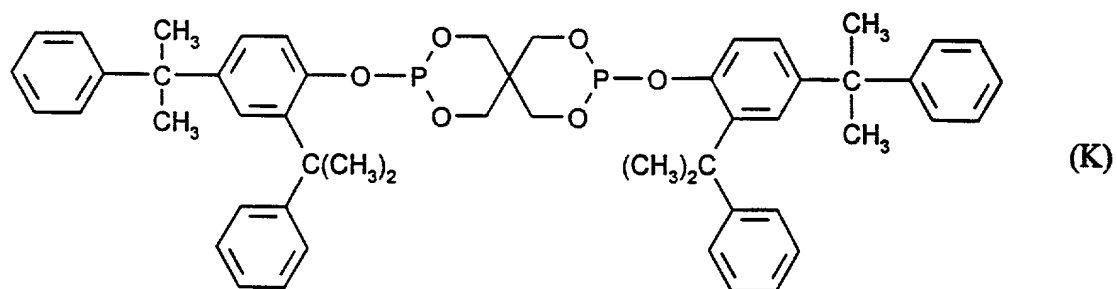
Z is a direct bond, methylene,  $-\text{C}(\text{R}_{16})_2-$  or sulfur, and

$\text{R}_{16}$  is  $\text{C}_1$ - $\text{C}_8$  alkyl.

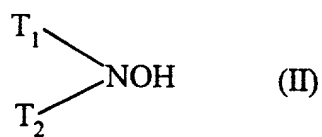
3. A process according to claim 1 wherein the organic phosphites and phosphonites of component (a) are selected from the group consisting of tris(2,4-di-tert-butylphenyl) phosphite, tris(nonylphenyl) phosphite and formulae (A), (B), (C), (D), (E), (F), (G), (H), (J), (K) and (L)







4. A process according to claim 1 wherein the hydroxylamine derivatives of component (i) are of the formula (II)



wherein

T<sub>1</sub> is straight or branched chain alkyl of 1 to 36 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 9 carbon atoms, or said aralkyl substituted by one or two alkyl of 1 to 12 carbon atoms or by one or two halogen atoms;

T<sub>2</sub> is hydrogen, or independently has the same meaning as T<sub>1</sub>.

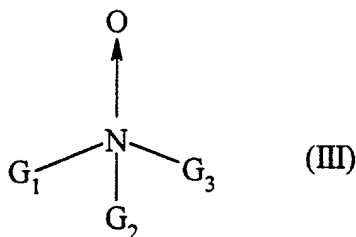
5. A process according to claim 4 wherein T<sub>1</sub> and T<sub>2</sub> are independently benzyl, ethyl, octyl, lauryl, dodecyl, tetradecyl, hexadecyl, heptadecyl or octadecyl.

6. A process according to claim 1 wherein the hydroxylamine derivatives of component (i) are selected from the group consisting of N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-didodecylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-tetradecylhydroxylamine, N-hexadecyl-N-heptadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, and N,N-di(hydrogenated tallow)hydroxylamine.

7. A process according to claim 1 wherein component (i) is an N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine.

8. A process according to claim 1 wherein the amine oxide derivatives of component (ii) are of the formula (III)





wherein

$\text{G}_1$  and  $\text{G}_2$  are independently a straight or branched chain alkyl of 6 to 36 carbon atoms, aryl of 6 to 12 carbon atoms, aralkyl of 7 to 36 carbon atoms, alkaryl of 7 to 36 carbon atoms, cycloalkyl of 5 to 36 carbon atoms, alkycycloalkyl of 6 to 36 carbon atoms or cycloalkylalkyl of 6 to 36 carbon atoms;

$\text{G}_3$  is a straight or branched chain alkyl of 1 to 36 carbon atoms, aryl of 6 to 12 carbon atoms, aralkyl of 7 to 36 carbon atoms, alkaryl of 7 to 36 carbon atoms, cycloalkyl of 5 to 36 carbon atoms, alkycycloalkyl of 6 to 36 carbon atoms or cycloalkylalkyl of 6 to 36 carbon atoms; with the proviso that at least one of  $\text{G}_1, \text{G}_2$  and  $\text{G}_3$  contains a  $\beta$  carbon-hydrogen bond; and

wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkycycloalkyl and cycloalkylalkyl groups may be interrupted by one to sixteen -O-, -S-, -SO-, -SO<sub>2</sub>-, -COO-, -OCO-, -CO-, -NG<sub>4</sub>-, -CONG<sub>4</sub>- and -NG<sub>4</sub>CO- groups, or wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkycycloalkyl and cycloalkylalkyl groups may be substituted by one to sixteen groups selected from -OG<sub>4</sub>, -SG<sub>4</sub>, -COOG<sub>4</sub>, -OCOG<sub>4</sub>, -COG<sub>4</sub>, -N(G<sub>4</sub>)<sub>2</sub>, -CON(G<sub>4</sub>)<sub>2</sub>, -NG<sub>4</sub>COG<sub>4</sub> and 5- and 6-membered rings containing the -C(CH<sub>3</sub>)(CH<sub>2</sub>R<sub>x</sub>)NL(CH<sub>2</sub>R<sub>x</sub>)(CH<sub>3</sub>)C- group or wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkycycloalkyl and cycloalkylalkyl groups are both interrupted and substituted by the groups mentioned above; and

wherein

G<sub>4</sub> is independently hydrogen or alkyl of 1 to 8 carbon atoms;

R<sub>x</sub> is hydrogen or methyl;

L is a C<sub>1-30</sub> straight or branched chain alkyl moiety, a -C(O)R moiety wherein R is a C<sub>1-30</sub> straight or branched chain alkyl group, or a -OR moiety wherein R is a C<sub>1-30</sub> straight or branched chain alkyl group; and

wherein said aryl groups may be substituted by one to three halogen, alkyl of 1 to 8 carbon atoms, alkoxy of 1 to 8 carbon atoms or combinations thereof.

9. A process according to claim 8 wherein wherein G<sub>1</sub> and G<sub>2</sub> are independently straight or branched chain alkyl groups of 6 to 22 carbon atoms and G<sub>3</sub> is a straight or branched chain alkyl of 1 to 22 carbon atoms.

10. A process according to claim 8 in which G<sub>3</sub> is methyl.

11. A process according to claim 8 wherein G<sub>1</sub> and G<sub>2</sub> are each independently a straight or branched chain alkyl of 12 to 22 carbon atoms and wherein G<sub>3</sub> is methyl.

12. A process according to claim 8 wherein G<sub>1</sub>, G<sub>2</sub> and G<sub>3</sub> are each independently a straight or branched chain alkyl of 12 to 22 carbon atoms.

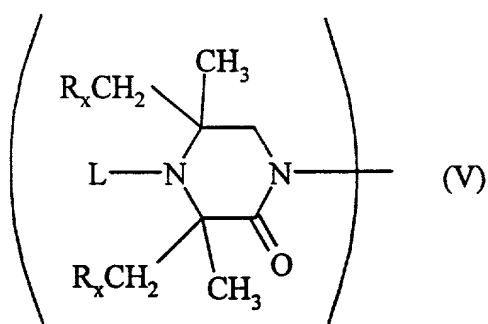
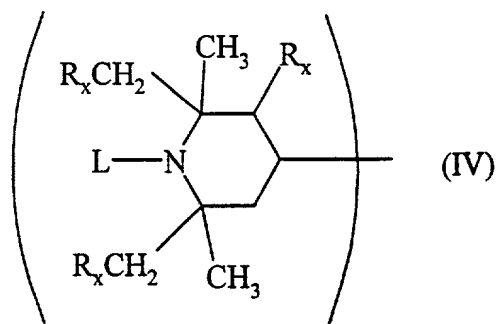
13. A process according to claim 8 wherein the amine oxide derivatives of component (ii) are selected from the group consisting of didecyl methyl amine oxide, tridecyl amine oxide, tridodecyl amine oxide and trihexadecyl amine oxide.

14. A process according to claim 8 wherein at least one of  $G_1$ ,  $G_2$  and  $G_3$  comprises at least one moiety of the group consisting of -O-, -S-, -SO-, -COO-, -CO- and -CONG<sub>4</sub>-.

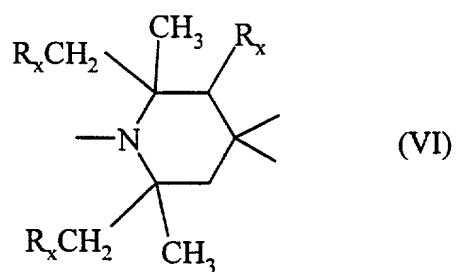
15. A process according to claim 1 wherein the amine oxide derivatives are poly(amine oxides).

16. A process according to claim 15 wherein the poly(amine oxides) comprise at least one moiety of the group consisting of -O-, -S-, -SO-, -COO-, -CO- and -CONG<sub>4</sub>-.

17. A process according to claim 8 wherein one or more of  $G_1$ ,  $G_2$  and  $G_3$  is substituted by one to sixteen groups of formulae (IV) and (V),

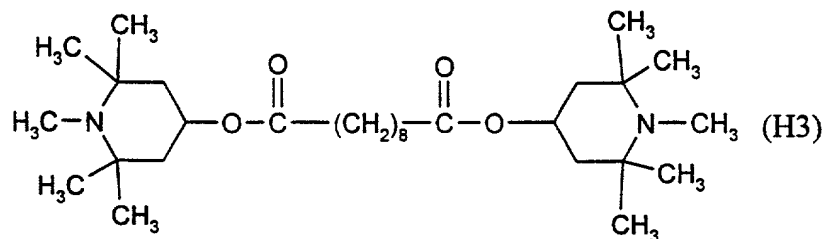
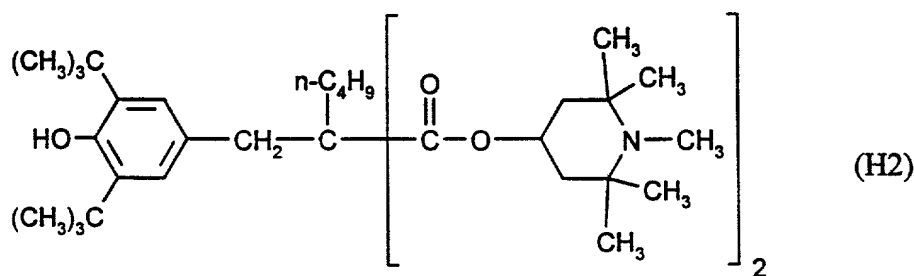
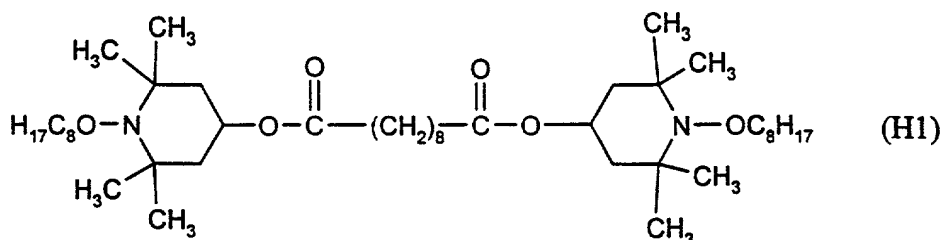


18. A process according to claim 1 wherein the hindered amine stabilizers of component (c) contain at least one group of the formula (VI)

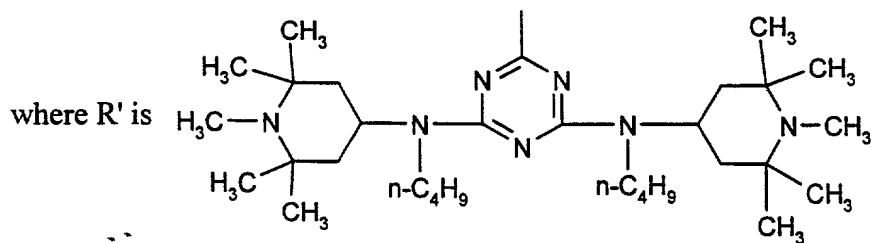
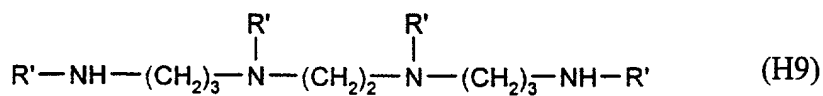
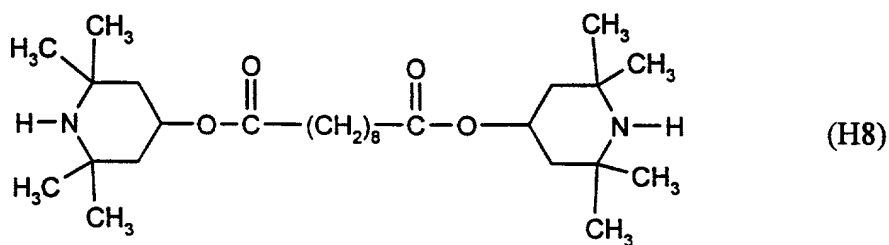
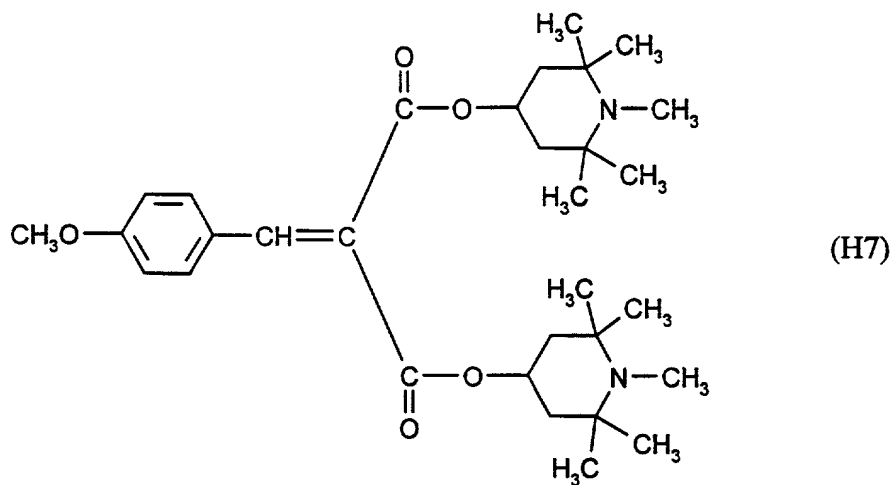


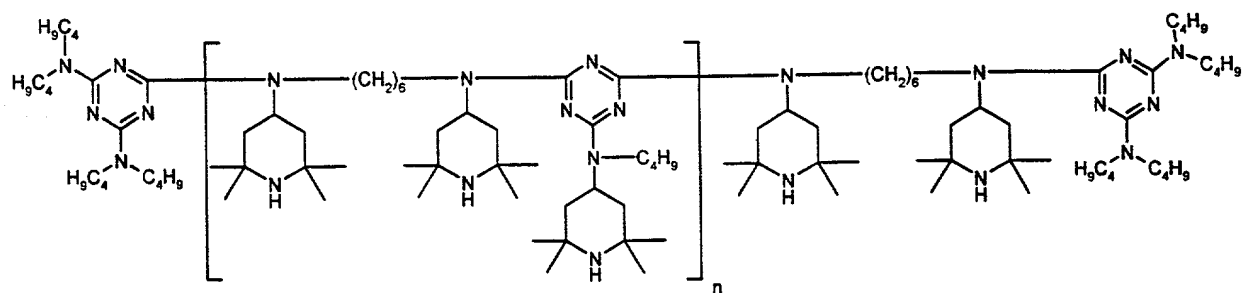
in which  $R_x$  is hydrogen or methyl.

19. A process according to claim 18 wherein the hindered amine stabilizers are selected from the group consisting of formulae (H1), (H2), (H3), (H4), (H5), (H6), (H7), (H8), (H9), (H10), (H11), (H12), (H13), (H14), (H15), (H16) and (H17)

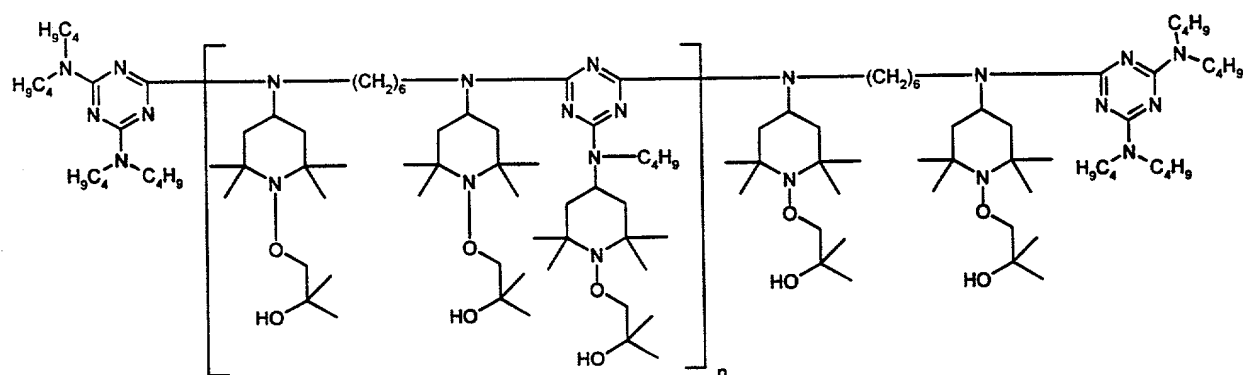




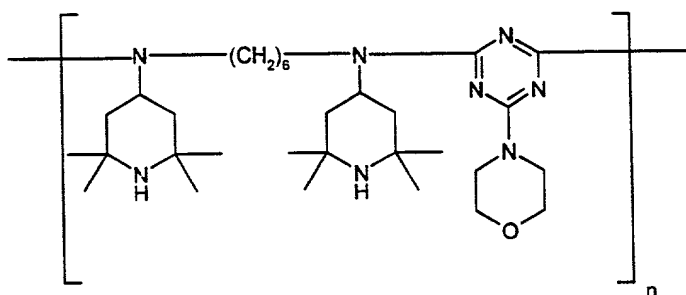




(H10)

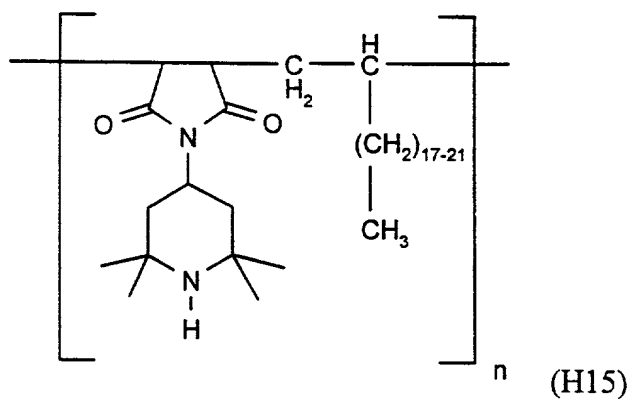
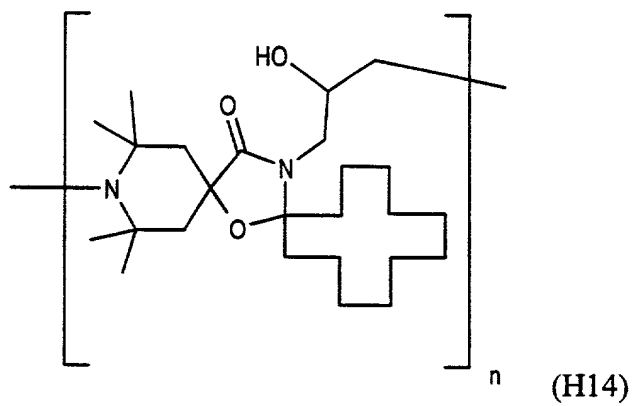
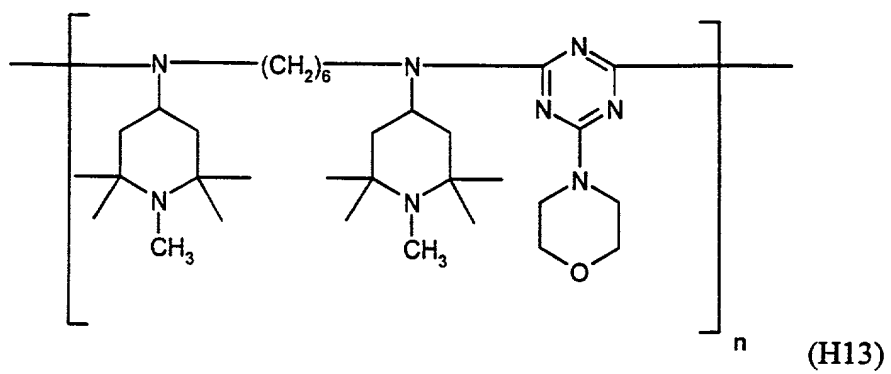


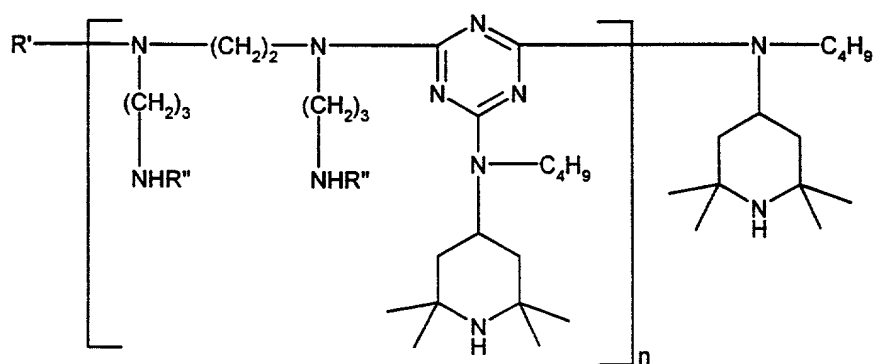
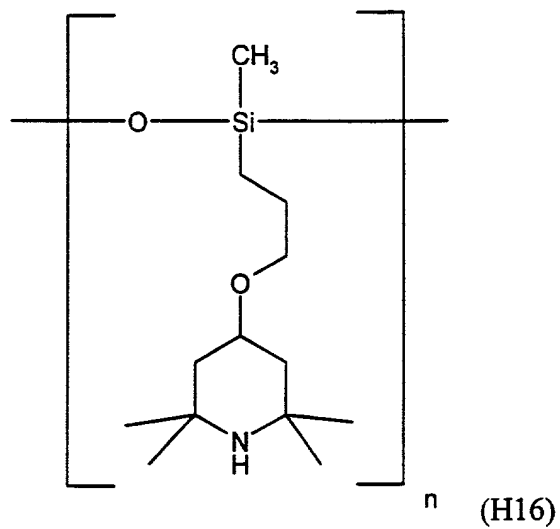
(H11)



(H12)

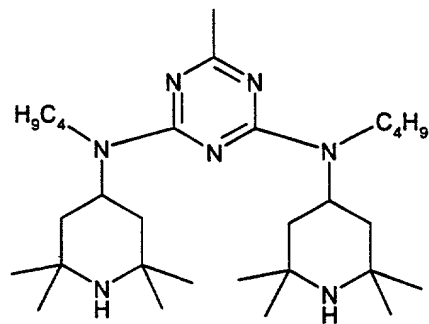






where  $R' = R''$  or H

and where  $R'' =$



(H17).

20. A process according to claim 1, wherein the temperature reaches the range from about 200°C to 400°C.